

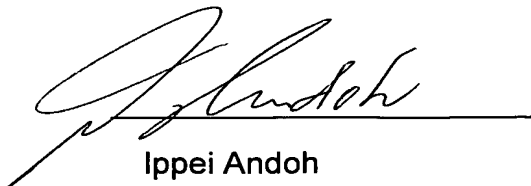
DECLARATION

I, Ippei Andoh, having an address of c/o CHEMPATENT, LTD., Tamura Bldg. 5th Floor, 4-23-17, Higashi-Ikebukuro, Toshima-ku, Tokyo, Japan, hereby declare that I have competent knowledge of the Japanese and English languages, and that I have made the accompanying translation of JAPANESE PATENT APPLICATION NO. 2002-354512 filed on December 6, 2002 in the name of JSR Corporation, and that the said translation is true and correct to the best of my knowledge and belief and that this declaration was made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code.

DECLARED by said Ippei Andoh

at Tamura Bldg. 5th Floor, 4-23-17, Higashi-Ikebukuro, Toshima-ku, Tokyo,
Japan

This 2nd day of March, 2007



Ippei Andoh

PATENT OFFICE
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the following application as filed with this Office.

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[List of Appended Documents]

[Document Name]	Specification 1
[Document Name]	Drawing 1
[Document Name]	Abstract 1
[Proof Requirement]	Requested[Document Name]

Specification

[Title of the Invention] Insulation film

[Claims]

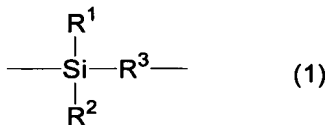
[Claim 1] An insulation film comprising an organosilicon polymer with a relative dielectric constant of 4 or less and having a dry etching selection ratio to the compound selected from the group consisting of silicon oxide, fluorine-doped silicon oxide, organosilicate glass, carbon-doped silicon oxide, methyl silsesquioxane, hydrogen silsesquioxane, spin-on-glass, polyorganosiloxane, and organic polymers.

[Claim 2] The insulation film according to claim 1, wherein the organosilicon polymer is a polycarbosilane.

[Claim 3] The insulation film according to claim 1, wherein the organosilicon polymer is at least one polymer selected from the group consisting of polymers having the structural unit of the following formula (1),

Formula (I):

[Chemical Formula 1]



wherein R¹ and R² independently represent a hydrogen atom, a substituted or unsubstituted alkyl group having 1-30 carbon atoms, a substituted or unsubstituted alkenyl group having 1-30 carbon atoms, a substituted or unsubstituted alkynyl group

having 1-30 carbon atoms, or a substituted or unsubstituted aromatic group and R^3 represents $-C\equiv C-$, $-CH_2-$ that may have a substituent linked with at least one $-C\equiv C-$ group, an alkylene group that may have a substituent having 2-30 carbon atoms linked with at least one $-C\equiv C-$ group, an alkenylene group that may have a substituent having 2-30 carbon atoms linked with at least one $-C\equiv C-$ group, an alkynylene group that may have a substituent having 2-30 carbon atoms linked with at least one $-C\equiv C-$ group, a divalent aromatic group that may have a substituent having 2-30 carbon atoms linked with at least one $-C\equiv C-$ group.

[Claim 4] A coating solution composition comprising (A) the organosilicon polymer described in claim 3 and (B) an organic solvent.

[Claim 5] A method of forming an insulation film comprising applying the coating solution composition of claim 4 to a substrate and heating the applied composition.

[Claim 6] A method of forming an insulation film comprising applying the coating solution composition of claim 4 to a substrate and heating the applied composition in the presence of oxygen or peroxide to three-dimensionally crosslink the composition and a three-dimensionally crosslinked insulation film.

[Claim 7] An etching stopper comprising the insulation film described in any one of claims 1, 2, 3, or 6 formed below an upper layer film comprising a compound selected from the group consisting of silicon oxide, fluorine-doped silicon oxide,

organosilicate glass, carbon-doped silicon oxide, methyl silsesquioxane, hydrogen silsesquioxane, spin-on glass, polyorganosiloxane, and an organic polymer, and having an etch rate of 1/3 or less the plasma dry etching rate of the upper layer film.

[Claim 8] A hard mask comprising the insulation film described in any one of claims 1, 2, 3, or 6 formed above a lower layer film comprising a compound selected from the group consisting of silicon oxide, fluorine-doped silicon oxide, organosilicate glass, carbon-doped silicon oxide, methyl silsesquioxane, hydrogen silsesquioxane, spin-on glass, polyorganosiloxane, and an organic polymer, and having an etch rate of 1/3 or less the plasma dry etching rate of the lower layer film.

[Claim 9] A method of dry etching an insulation film characterized by using either the etching stopper of claim 7 or the hard mask of claim 8, or both.

[Claim 10] A damascene structure processing method characterized by using either the etching stopper of claim 7 or the hard mask of claim 8, or both.

[Claim 11] A dual damascene structure processing method characterized by using either the etching stopper of claim 7 or the hard mask of claim 8, or both.

[Detailed Description of the Invention]

[0001]

[Field of the Invention]

The present invention relates to an etching stopper and a hard mask. More particularly, the present invention relates to an etching stopper and a hard mask preferably used in a dry etching process of interlayer dielectric films made of a material such as SiO₂, fluorine-doped SiO₂, organic or inorganic SOG (spin-on glass), or Low-k films, or in a dry etching process of barrier films such as SiN films, SiC films, or SiCN films in the manufacture of semiconductor devices.

[0002]

[Prior Art]

Conventionally, interlayer dielectric films and barrier films used in the manufacture of semiconductor devices have been processed by dry etching using a gas containing a halogen-containing gas as a major component. SiN (silicon nitride) films, SiC (silicon carbide) films, SiCN (carbonized silicon nitride) films, and the like formed by plasma CVD are mainly used as a hard mask or etching stopper for SiO₂ materials, fluorine-doped SiO₂ materials, organic inorganic SOG (spin-on glass) materials, low dielectric interlayer dielectric films, and the like. These types of hard masks and etching stoppers have a high dielectric constant of 4 or more. If applied to high-speed devices that are processed in combination with the technique of low dielectric interlayer dielectric films such as FSG films, OSG films, and porous Low-k films and the copper

wiring technique, these hard masks and etching stoppers have been reported to require a high actual dielectric constant for the dielectric layer that makes it difficult to improve delayed transmission and the like. Therefore, development of a material having a dielectric constant of less than 4 and exhibiting a high etching selection ratio to materials such as SiO₂, fluorine-doped SiO₂, organic or inorganic SOG (Spin-on glass) material, Low-k films, and interlayer dielectric films used with SiN, SiC, or SiCN has been strongly desired.

[0003]

(Patent Document 1)

Japanese Patent Application Laid-open No. 2002-76115

[0004]

[Problems to be Solved by the Invention]

The present invention solves the above-mentioned problems in prior art and provides a thin film material which has a etching selection ratio in the combination with a material such as SiO₂, fluorine-doped SiO₂, organic or inorganic SOG (spin-on glass), or an interlayer dielectric film such as a Low-k film and can effectively function as an etching stopper and a hard mask, and a processing method of a damascene structure or a dual damascene structure using the etching stopper and the hard mask.

[0005]

[Means for Solving the Problem]

In the present invention, an insulation film comprising an organosilicon polymer having a relative dielectric constant of 4 or less is used as an etching stopper or a hard mask. If this

organosilicon polymer is used as an etching stopper or a hard mask in the damascene process of a film comprising a compound selected from the group consisting of silicon oxide, fluorine-doped silicon oxide, organosilicate glass, carbon-doped silicon oxide, methyl silsesquioxane, hydrogen silsesquioxane, spin-on-glass, polyorganosiloxane, and an organic polymer, precision of the configuration obtained by the process in the final stage can be increased and the actual dielectric constant after wiring processing can be reduced.

[0006]

[Preferred Embodiment of the Invention]

(A) Organosilicon polymer

The insulation film of the present invention comprises an organosilicon polymer having a relative dielectric constant of 4 or less.

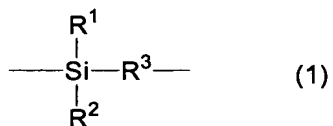
Polycarbosilane having a relative dielectric constant of 4 or less, preferably 3.5 or less, can be given as such an organosilicon polymer.

A particularly preferable organosilicon polymer is a polymer (hereinafter referred to as "Polymer (1)") having a recurring unit of the following formula (1):

Formula (I):

[0007]

[Chemical Formula 2]



wherein R¹ and R² independently represent a hydrogen atom, a substituted or unsubstituted alkyl group having 1-30 carbon atoms, a substituted or unsubstituted alkenyl group having 1-30 carbon atoms, a substituted or unsubstituted alkynyl group having 1-30 carbon atoms, or a substituted or unsubstituted aromatic group and R³ represents -C≡C-, -CH₂- that may have a substituent linked with at least one -C≡C- group, an alkylene group that may have a substituent having 2-30 carbon atoms linked with at least one -C≡C- group, an alkenylene group that may have a substituent having 2-30 carbon atoms linked with at least one -C≡C- group, an alkynylene group that may have a substituent having 2-30 carbon atoms linked with at least one -C≡C- group, a divalent aromatic group that may have a substituent having 2-30 carbon atoms linked with at least one -C≡C- group.

[0008]

As examples of the substituted or unsubstituted alkyl group having 1-30 carbon atoms represented by R¹ or R², a methyl group, ethyl group, propyl group, hexyl group, cyclohexyl group, octyl group, dodecanyl group, trifluoromethyl group, 3,3,3-trifluoropropyl group, chloromethyl group, aminomethyl group, hydroxymethyl group, silylmethyl group, and 2-methoxyethyl group can be given; as examples of the

substituted or unsubstituted alkenyl group having 1-30 carbon atoms, a vinyl group, 2-propenyl group, isopropenyl group, 3-butenyl group, 5-hexenyl group, 1,3-butadienyl group, and 3,3,3-trifluoro-1-propenyl group can be given; as examples of the substituted or unsubstituted alkynyl group having 1-30 carbon atoms, an ethynyl group, 1-propynyl group, 2-propynyl group, butynyl group, trimethylsilylethynyl group, and phenylethynyl group can be given; and as examples of the substituted or unsubstituted aromatic group, a phenyl group, naphthyl group, pyrazinyl group, 4-methylphenyl group, 4-vinylphenyl group, 4-ethynylphenyl group, 4-aminophenyl group, 4-chlorophenyl group, 4-hydroxyphenyl group, 4-carboxyphenyl group, 4-methoxyphenyl group, and 4-silylphenyl group can be given. As examples of the $-CH_2-$ group that may have a substituent linked with at least one $-C=C-$ group represented by R^3 , a methylene group and fluoromethylene group linked with one or two $-C=C-$ groups can be given; as examples of the alkylene group that may have a substituent having 2-30 carbon atoms linked with at least one $-C=C-$ group, an ethylene group, propylene group, tetramethylene group, and tetrafluoroethylene group linked with one or two $-C=C-$ groups can be given; as examples of the alkenylene group that may have a substituent having 2-30 carbon atoms linked with at least one $-C=C-$ group, a vinylene group, propenylene group, and butadienylene group linked with one or two $-C=C-$ groups can be given; as examples of the alkynylene group that may have a substituent having 2-30 carbon atoms linked with at least one

-C=C- group, an ethynylene group, propenylene group, and butynylene group linked with at least one -C=C- group can be given; as examples of the aromatic group that may have a substituent linked with at least one -C=C- group, a phenylene group, naphthylene group, biphenylene group, anthracenedyl group, pyridydenedyl group, thiophendilyl group, fluorophenylene group, chlorophenylene group, methylphenylene group, silylphenylene group, hydroxyphenylene group, aminophenylene group, phenylene methylene phenylene group, phenyleneoxyphenylene group, phenylenepropylidenephenylene group, and phenylene(hexafluoropropylidene)phenylene group linked with one or two -C=C- groups can be given.

[0009]

The silicon-containing polymer compound represented by the formula (1) used in the present invention is specifically a compound having the following recurring units:

silylene-ethynylene,
methyl silylene-ethynylene,
phenyl silylene-ethynylene,
silylene-ethynylene-1,3-phenylene-ethynylene,
silylene-ethynylene-1,4-phenylene-ethynylene,
silylene-ethynylene-1,2-phenylene-ethynylene,
methyl silylene-ethynylene-1,3-phenylene-ethynylene,
methyl silylene-ethynylene-1,4-phenylene-ethynylene,
methyl silylene-ethynylene-1,2-phenylene-ethynylene,
dimethyl silylene-ethynylene-1,3-phenylene-ethynylene,
dimethyl silylene-ethynylene-1,4-phenylene-ethynylene,

dimethyl silylene-ethynylene-1,2-phenylene-ethynylene,
diethyl silylene-ethynylene-1,3-phenylene-ethynylene,
phenyl silylene-ethynylene-1,3-phenylene-ethynylene,
phenyl silylene-ethynylene-1,4-phenylene-ethynylene,
phenyl silylene-ethynylene-1,2-phenylene-ethynylene,
diphenyl silylene-ethynylene-1,3-phenylene-ethynylene,
hexyl silylene-ethynylene-1,3-phenylene-ethynylene,
vinyl silylene-ethynylene-1,3-phenylene-ethynylene,
ethynyl silylene-ethynylene-1,3-phenylene-ethynylene,
2-propenyl silylene-ethynylene-1,3-phenylene-ethynylene,
2-propynyl silylene-ethynylene-1,3-phenylene-ethynylene,
trifluoromethyl
silylene-ethynylene-1,3-phenylene-ethynylene,
3,3,3-trifluoropropyl
silylene-ethynylene-1,3-phenylene-ethynylene,
4-methylphenyl
silylene-ethynylene-1,3-phenylene-ethynylene,
4-vinylphenyl silylene-ethynylene-1,3-phenylene-ethynylene,
4-ethynylphenyl silylene-ethynylene-1,3-phenylene-
ethynylene,
phenylethynyl silylene-ethynylene-1,3-phenylene-ethynylene,
silylene-ethynylene(5-methyl-1,3-phenylene)ethynylene,
phenyl silylene-ethynylene(5-methyl-1,3-phenylene)-
ethynylene,
phenyl silylene-ethynylene(5-silyl-1,3-phenylene)-
ethynylene,
phenyl silylene-ethynylene(5-hydroxy-1,3-phenylene)-

ethynylene,
phenyl silylene-ethynylene-2,7-naphthylene-ethynylene,
silylene-ethynylene-5,10-anthracerylene-ethynylene,
phenyl silylene-ethynylene-4,4'-biphenylene-ethynylene,
phenyl silylene-ethynylene-1,4-phenylenemethylene-1',4'-
phenylene-ethynylene,
phenyl silylene-ethynylene-1,4-phenylene-2,2-propylidene-
1',4'-phenylene-ethynylene,
phenyl silylene-ethynylene-1,4-phenylene-2,2-(1,1,1,3,3,3-
hexafluoropropylidene)-1',4'-phenylene-ethynylene,
phenyl silylene-ethynylene-1,4-phenyleneoxy-1',4'-
phenylene-ethynylene,
phenyl silylene-ethynylene-2,5-pyridylene-ethynylene,
phenyl silylene-ethynylene 2,5-thiophenylene-ethynylene,
methyl silylene-ethynylene methylene-ethynylene,
phenyl silylene-1,4-phenylene(phenylsilylene)ethynylene-
1',3-phenylene-ethylynylene,
phenylsilyleneoxy(phenylsilylene)ethynylene,
phenylsilyleneoxy(phenylsilylene)ethynylene-1',4'-phenylene
-ethynylene,
phenylsilyleneimino(phenylsilylene)ethynylene-1',3'-
phenylene-ethynylene,
phenylsilyleneimino(phenylsilylene)ethynylene-1',4'-
phenylene-ethynylene,
silylene-1,3-phenylene-ethynylene,
silylene-1,4-phenylene-ethynylene,
silylene-1,2-phenylene-ethynylene,

phenylsilylene-1,3-phenylene-ethynylene,
phenylsilylene-1,4-phenylene-ethynylene,
phenylsilylene-1,2-phenylene-ethynylene,
diphenylsilylene-1,3-phenylene-ethynylene,
methylsilylene-1,3-phenylene-ethynylene,
methylsilylene-1,4-phenylene-ethynylene,
methylsilylene-1,2-phenylene-ethynylene,
dimethylsilylene-1,3-phenylene-ethynylene,
diethylsilylene-1,3-phenylene-ethynylene,
phenylsilylene-1,3-butadienylene,
diphenylsilylene-1,3-butadienylene,
phenylsilylene-methylene-ethynylene,
diphenylsilylene-methylene-ethynylene-methylene,
phenylsilylene-methylene-ethynylene-methylene,
silylene-1,4-phenylene-ethynylene-1',4'-phenylene,
methylsilylene-1,4-phenylene-ethynylene-1',4'-phenylene,
dimethylsilylene-1,4-phenylene-ethynylene-1',4'-phenylene,
and
phenylsilylene-1,4-phenylene-ethynylene-1',4'-phenylene.

Although there are no specific limitations, the average molecular weight of the organic silicon polymer of the formula (1) is preferably 500-500,000. These silicon-containing polymer compounds are solid or liquid at the atmospheric temperature.

Although there are no specific limitations, the average molecular weight of the organic silicon polymer of the formula (1) is preferably 500-500,000. These silicon-containing

polymer compounds are solid or liquid at the atmospheric temperature.

[0010]

The method for producing the organosilicon polymer of the formula (1) includes, but are not limited to a dehydrogenation copolymerization method of a diethynyl compound and a silane compound using a basic oxide, metal hydride, or a metal compound as a catalyst (Japanese Patent Applications Laid-open No. 7-90085, No. 10-120689, and No. 11-158187), a dehydrogenation polymerization method of an ethynyl silane compound using a basic oxide as a catalyst (Japanese Patent Applications Laid-open No. 9-143271), a method of reacting an organomagnesium reagent with a dichlorosilane (Japanese Patent Applications Laid-open No. 7-102069 and No. 11-029579), a dehydrogenation copolymerization method of a diethynyl compound and a silane compound using a cuprous chloride and tertiary amine as a catalyst (Hua Qin Liu and John F. Harrod, The Canadian Journal of Chemistry, Vol. 68, 1100-1105 (1990)), and a dehydrogenation copolymerization method of a diethynyl compound and a silane compound using magnesium oxide as a catalyst (Japanese Patent Applications Laid-open No. 7-90085 and No. 10-204181).

[0011]

(B) Organic solvent

The film-forming composition of the present invention is usually a solution or a dispersion of the component (A) in an organic solvent (B).

As the organic solvent (B), at least one solvent selected from the group consisting of ketone solvents, amide solvents, ester solvents, aliphatic hydrocarbon solvents, aromatic solvents, and halogen-containing solvents can be used.

[0012]

As examples of the ketone solvent, acetone, methyl ethyl ketone, methyl n-propyl ketone, methyl n-butyl ketone, diethyl ketone, methyl i-butyl ketone, methyl n-pentyl ketone, ethyl n-butyl ketone, methyl n-hexyl ketone, di-i-butyl ketone, trimethylenonane, cyclopentanone, cyclohexanone, cycloheptanone, cyclooctanone, 2-hexanone, methylcyclohexanone, 2,4-pentanedione, acetonylacetone, diacetone alcohol, acetophenone, fenchone, and the like can be given.

These ketone solvents may be used either individually or in combination of two or more.

[0013]

As the amide solvent, nitrogen-containing solvents such as N,N-dimethylimidazolidinone, N-methylformamide, N,N-dimethylformamide, N,N-dimethylformamide, acetamide, N-methylacetamide, N,N-dimethylacetamide, N-methylpropionamide, N-methylpyrrolidone, and the like can be given.

These amide solvents may be used either individually or in combination of two or more.

[0014]

As examples of the ether solvent, ethyl ether, i-propyl ether,

n-butyl ether, n-hexyl ether, 2-ethylhexyl ether, ethylene oxide, 1,2-propylene oxide, dioxolane, 4-methyl dioxolane, dioxane, dimethyl dioxane, ethylene glycol monomethyl ether, ethylene glycol dimethyl ether, ethylene glycol monoethyl ether, ethylene glycol diethyl ether, ethylene glycol mono-n-butyl ether, ethylene glycol mono-n-hexyl ether, ethylene glycol monophenyl ether, ethylene glycol mono-2-ethyl butyl ether, ethylene glycol dibutyl ether, diethylene glycol monomethyl ether, diethylene glycol dimethyl ether, diethylene glycol monoethyl ether, diethylene glycol diethyl ether, diethylene glycol mono-n-butyl ether, diethylene glycol di-n-butyl ether, diethylene glycol mono-n-hexyl ether, ethoxy triglycol, tetraethylene glycol di-n-butyl ether, propylene glycol monomethyl ether, propylene glycol monoethyl ether, propylene glycol monopropyl ether, propylene glycol monobutyl ether, dipropylene glycol monomethyl ether, dipropylene glycol monoethyl ether, tripropylene glycol monomethyl ether, tetrahydrofuran, 2-methyltetrahydrofuran, diphenyl ether, anisole, and the like can be given.

These ether solvents may be used either individually or in combination of two or more.

[0015]

As examples of the ester solvent, diethyl carbonate, propylene carbonate, methyl acetate, ethyl acetate, gamma-butyrolactone, gamma-valerolactone, n-propyl acetate, i-propyl acetate, n-butyl acetate, i-butyl acetate, sec-butyl acetate, n-pentyl acetate, sec-pentyl acetate, 3-methoxybutyl acetate,

methylpentyl acetate, 2-ethylbutyl acetate, 2-ethylhexyl acetate, benzyl acetate, cyclohexyl acetate, methylcyclohexyl acetate, n-nonyl acetate, methyl acetoacetate, ethyl acetoacetate, ethylene glycol monomethyl ether acetate, ethylene glycol monoethyl ether acetate, diethylene glycol monomethyl ether acetate, diethylene glycol monoethyl ether acetate, diethylene glycol mono-n-butyl ether acetate, propylene glycol monomethyl ether acetate, propylene glycol monoethyl ether acetate, propylene glycol monopropyl ether acetate, propylene glycol monobutyl ether acetate, dipropylene glycol monomethyl ether acetate, dipropylene glycol monoethyl ether acetate, glycol diacetate, methoxy triglycol acetate, ethyl propionate, n-butyl propionate, i-amyl propionate, diethyl oxalate, di-n-butyl oxalate, methyl lactate, ethyl lactate, n-butyl lactate, n-amyl lactate, diethyl malonate, dimethyl phthalate, diethyl phthalate, and the like can be given.

These ester solvents may be used either individually or in combination of two or more. As examples of the aliphatic hydrocarbon solvent, n-pentane, i-pentane, n-hexane, i-hexane, n-heptane, i-heptane, 2,2,4-trimethylpentane, n-octane, i-octane, cyclohexane, methylcyclohexane, and the like can be given.

These aliphatic hydrocarbon solvents may be used either individually or in combination of two or more.

[0016]

As examples of the aromatic hydrocarbon solvent, benzene,

toluene, xylene, ethylbenzene, trimethylbenzene, methylethylbenzene, n-propylebenzene, i-propylebenzene, diethylbenzene, i-butylbenzene, triethylbenzene, di-i-propylbenzene, n-amyl naphthalene, trimethylbenzene, and the like can be given.

These aromatic hydrocarbon solvents may be used either individually or in combination of two or more. As examples of the halogen-containing solvent, dichloromethane, chloroform, fluorocarbon, chlorobenzene, dichlorobenzene, and the like can be given.

An organic solvent with a boiling point of 250°C or less is preferable in the present invention. As the type of solvent, ketones, esters, and aromatic hydrocarbons solvents are particular preferable. Either one type or two or more types among these solvents may be preferably used.

[0017]

Other additives

The film-forming composition of the present invention may further comprise other components such as a curing promoter, colloidal silica, colloidal alumina, organic polymer, surfactant, silane coupling agent, and triazene compound.

[0018]

As the thermal polymerization initiator, an organic peroxide can be used. As specific examples of the organic peroxide, BPO (benzoyl peroxide), Pertetra A, Percumyl D (dicumyl peroxide), BTTB (3,3',4,4'-tetrabutylperoxycarbonyl benzophenone) (all manufactured by NOF Corporation), and the like can be given.

Organic azo compounds such as 2,2'-azobisisobutyronitrile (AIBN), dimethyl-2,2'-azobis(2-methylpropionate) (V-601, manufactured by Wako Pure Chemical Industries, Ltd.), 1,1'-azobis(1-acetoxy-1-phenylethane) (OT(azo)-15, manufactured by the Otsuka Chemical Co., Ltd.), and the like are also effective.

The amount of the promoter for hydrosilylation to be added is 0.1-50 parts by weight, and preferably 1-30 parts by weight, for 100 parts by weight of the film-forming composition.

[0019]

Colloidal silica is a dispersion of high purity silicic anhydride in a hydrophilic organic solvent, for example, with a solid content of about 10-40 wt%, wherein silica particles with an average diameter of 5-30 micrometers, and preferably 10-20 micrometers, are dispersed. Such colloidal silica is commercially available, for example, as methanol silica sol or iso-propanol silica sol (manufactured by Nissan Chemical Industries, Ltd.) or Oscal™ (manufactured by Catalysts & Chemicals Ind. Co., Ltd.).

The above colloidal alumina is commercially available, for example, as Alumina Sol 520™, Alumina Sol 100™, or Alumina Sol 200™ (manufactured by Nissan Chemical Industries, Ltd.), and Alumina Clear Sol™, Alumina Sol 10™, or Alumina Sol 132™ (manufactured by Kawaken Fine Chemicals Co., Ltd.).

[0020]

As examples of the organic polymer, a polymer having a sugar chain structure, vinyl amide polymer, (meth)acrylic polymer,

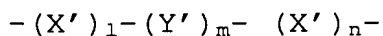
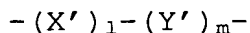
aromatic vinyl compound polymer, dendrimer, polyimide, polyamic acid, polyarylene, polyamide, polyquinoxaline, polyoxadiazole, fluorine polymer, polymer having a polyalkylene oxide structure, and the like can be given.

[0021]

As the polyalkylene oxide structure, a polymethylene oxide structure, polyethylene oxide structure, polypropylene oxide structure, polytetramethylene oxide structure, polybutylene oxide structure, and the like can be given.

As specific examples of the compound having a polyalkylene oxide structure, ether compounds such as polyoxymethylene alkyl ether, polyoxyethylene alkyl ether, polyoxyethylene alkylphenyl ether, polyoxyethylene sterol ether, polyoxyethylene lanolin derivatives, ethylene oxide derivatives of alkylphenol formalin condensate, polyoxyethylene polyoxypropylene block copolymers, and polyoxyethylene polyoxypropylene alkyl ethers; ether-ester compounds such as polyoxyethylene glyceride, polyoxyethylene sorbitan fatty acid ester, polyoxyethylene sorbitol fatty acid ester, and polyoxyethylene fatty acid alkanolamide sulfate; and ester compounds such as polyethylene glycol fatty acid ester, ethylene glycol fatty acid ester, fatty acid monoglyceride, polyglycerol fatty acid ester, sorbitan fatty acid ester, propylene glycol fatty acid ester, and sucrose fatty acid ester, and the like can be given.

As a polyoxyethylene polyoxypropylene block copolymer, compounds having the following block structure can be given.



wherein X' indicates a group $-\text{CH}_2\text{CH}_2\text{O}-$, Y' indicates a group $-\text{CH}_2\text{CH}(\text{CH}_3)\text{O}-$, l is an integer of 1-90, m is an integer of 10-99, and n is an integer of 0-90.

[0022]

Of these, the ether compounds such as a polyoxyethylene alkyl ether, polyoxyethylene-polyoxypropylene block copolymer, polyoxyethylene polyoxypropylene alkyl ether, polyoxyethylene glyceride, polyoxyethylene sorbitan fatty acid ester, and polyoxyethylene sorbitol fatty acid ester are preferable.

The surfactants may be used either individually or in combination of two or more.

[0023]

As examples of the surfactant, a nonionic surfactant, anionic surfactant, cationic surfactant, amphoteric surfactant, and the like can be given. The surfactant may be a fluorine-containing surfactant, silicone surfactant, polyalkylene oxide surfactant, poly(meth)acrylate surfactant, or the like. Of these, the fluorine-containing surfactant and the silicone surfactant are preferable.

[0024]

As examples of the fluorine-containing surfactant, compounds in which at least the terminal, the main chain, or the side chain includes a fluoroalkyl or fluoroalkylene group, such as 1,1,2,2-tetrafluorooctyl(1,1,2,2-tetrafluoropropyl)ether, 1,1,2,2-tetrafluorooctylhexyl ether, octaethylene glycol

di(1,1,2,2-tetrafluorobutyl) ether, hexaethylene glycol
(1,1,2,2,3,3-hexafluoropentyl) ether, octapropylene glycol
di(1,1,2,2-tetrafluorobutyl) ether, hexapropylene glycol
di(1,1,2,2,3,3-hexafluoropentyl) ether, sodium
perfluorododecylsulfonate,
1,1,2,2,8,8,9,9,10,10-decafluorododecane,
1,1,2,2,3,3-hexafluorodecane,
N-3-(perfluorooctanesulfonamide)-propyl-N,N'-dimethyl-N-
carboxymethylene ammonium betaine, perfluoroalkyl sulfonamide
propyltrimethyl ammonium salt,
perfluoroalkyl-N-ethylsulfonylglycine salt,
bis(N-perfluorooctylsulfonyl-N-ethylaminoethyl) phosphate,
and monoperfluoroalkylethyl phosphate can be given.

As examples of commercially available products of the
fluorine-containing surfactant, Megafac F142D, F172, F173,
F183 (manufactured by Dainippon Ink and Chemicals, Inc.), Eftop
EF301, EF303, EF352 (manufactured by Shin-Akita Kasei Co.,
Ltd.). Fluorad FC-430, FC-431 (manufactured by Sumitomo 3M,
Ltd.), Asahi Guard AG710, Surflon S-382, SC-101, SC-102, SC-103,
SC-104, SC-105, SC-106 (manufactured by Asahi Glass Co., Ltd.),
BM-1000, BM-1100 (manufactured by BM Chemie), NBX-15
(manufactured by NEOS Co., Ltd.), and the like can be given.
Of these, Megafac F172, BM-1000, BM-1100, and NBX-15 are
preferable.

[0025]

As the silicone surfactant, SH7PA, SH21PA, SH28PA, SH30PA,
ST94PA (manufactured by Toray-Dow Corning Silicone Co., Ltd.)

and the like may be used. Of these, SH28PA and SH30PA are preferable.

The surfactant is used in an amount of usually 0.00001 to 1 part by weight for 100 parts by weight of the polymer formed of the component (A) and the component (B).

The surfactants may be used either individually or in combination of two or more.

[0026]

As examples of the silane coupling agent,
3-glycidyloxypropyltrimethoxysilane,
3-aminoglycidyloxypropyltriethoxysilane, 3-methacryloxypropyl
trimethoxysilane, 3-glycidyloxypropylmethyldimethoxysilane,
1-methacryloxypropylmethyldimethoxysilane,
3-aminopropyltrimethoxysilane, 3-aminopropyltriethoxysilane,
2-aminopropyltrimethoxysilane, 2-aminopropyltriethoxysilane,
N-(2-aminoethyl)-3-aminopropyltrimethoxysilane,
N-(2-aminoethyl)-3-aminopropylmethyldimethoxysilane,
3-ureidopropyltrimethoxysilane,
3-ureidopropyltriethoxysilane,
N-ethoxycarbonyl-3-aminopropyltrimethoxysilane,
N-ethoxycarbonyl-3-aminopropyltriethoxysilane,
N-triethoxysilylpropyltriethylenetriamine,
N-triethoxysilylpropyltriethylenetriamine,
10-trimethoxysilyl-1,4,7-triazadecane,
10-triethoxysilyl-1,4,7-triazadecane,
9-trimethoxysilyl-3,6-diazanonylacetate,
9-triethoxysilyl-3,6-diazanonylacetate,

N-benzyl-3-aminopropyltrimethoxysilane,
N-benzyl-3-aminopropyltriethoxysilane,
N-phenyl-3-aminopropyltrimethoxysilane,
N-phenyl-3-aminopropyltriethoxysilane,
N-bis(oxyethylene)-3-aminopropyltrimethoxysilane,
N-bis(oxyethylene)-3-aminopropyltriethoxysilane, and the
like can be given.

The surfactants may be used either individually or in
combination of two or more.

[0027]

The following compounds can be given as examples of triazene
compounds: 1,2-bis(3,3-dimethyltriazenyl)benzene,
1,3-bis(3,3-dimethyltriazenyl)benzene,
1,4-bis(3,3-dimethyltriazenyl)benzene,
bis(3,3-dimethyltriazenylphenyl)ether,
bis(3,3-dimethyltriazenylphenyl)methane,
bis(3,3-dimethyltriazenylphenyl)sulfone,
bis(3,3-dimethyltriazenylphenyl)sulfide,
2,2-bis[4-(3,3-dimethyltriazenylphenoxy)phenyl]-1,1,1,3,3,3
-hexafluoropropane,
2,2-bis[4-(3,3-dimethyltriazenylphenoxy)phenyl]propane,
1,3,5-tris(3,3-dimethyltriazenyl)benzene,
2,7-bis(3,3-dimethyltriazenyl)-9,9-bis[4-(3,3-dimethyltriaz
enyl)phenyl]fluorene,
2,7-bis(3,3-dimethyltriazenyl)-9,9-bis[3-methyl-4-
(3,3-dimethyltriazenyl)-phenyl]fluorene,
2,7-bis(3,3-dimethyltriazenyl)-9,9-bis[3-phenyl-4-

(3,3-dimethyltriazenyl)phenyl]-fluorene,
2,7-bis(3,3-dimethyltriazenyl)-9,9-bis[3-propenyl-4-(3,3-dimethyltriazenyl)phenyl]-fluorene,
2,7-bis(3,3-dimethyltriazenyl)-9,9-bis[3-fluoro-4-(3,3-dimethyltriazenyl)phenyl]-fluorene,
2,7-bis(3,3-dimethyltriazenyl)-9,9-bis[3,5-difluoro-4-(3,3-dimethyltriazenyl)phenyl]-fluorene, and
2,7-bis(3,3-dimethyltriazenyl)-9,9-bis[3-trifluoromethyl-4-(3,3-dimethyltriazenyl)-phenyl]fluorene.

The surfactants may be used either individually or in combination of two or more.

[0028]

The total solid content in the film-forming composition of the present invention may be appropriately adjusted according to the target application, preferably, in the range of 1-30 wt%. The total solid content in the range of 1-30 wt% not only ensures production of a coated film thickness in an appropriate range, but also ensures excellent storage stability of the composition.

[0029]

When the composition of the present invention is applied to a substrate, a coating method such as spin coating, dip coating, roll coating, spray coating, or scan coating can be used.

[0030]

A coated film with a dry thickness of about 0.01-1.5 micrometers is obtained by a single application, and about 0.2-3

micrometers is obtained by one additional application of the composition of the present invention. The coated film is then dried at an ordinary temperature or by heating at about 80-600°C for 5-240 minutes, thereby forming the coated film (cure film) that can be used as an interlayer dielectric film. A hot plate, oven, furnace, or the like can be used for heating the coated film in air, in nitrogen or argon, under vacuum, or under reduced pressure in which oxygen concentration is controlled. If heated particularly at 100-450°C for 1-240 minutes in the presence of oxygen, a three-dimensional cross-linking structure in which oxygen atoms are introduced in carbosilane can be formed. If the three-dimensional cross-linking structure is formed, the polycarbosilane becomes insoluble in solvents and is maintained stable during fabrication processing with heating or the like. The three-dimensional cross-linking structure can also be formed by adding a peroxide, diazo compound, or the like to the coating composition and heating the composition instead of curing in the presence of oxygen. The coated film can also be cured by irradiating active energy rays such as electron beams or ultraviolet rays.

[0031]

The organosilicon polymer can be preferably used in combination with a silicon oxide-based interlayer dielectric film such as silicon oxide (SiO_2), fluorine-doped silicon oxide (FSG), organosilicate glass (OCG), carbon-doped silicon oxide (SiOC), methyl silsesquioxane (MSQ), hydrogen silsesquioxane (HSQ), spin-on-glass (SOG), or polyorganosiloxane or in

combination with an organic polymer (A)-based interlayer dielectric film such as polyarylene, polyarylene ether, polyimide, or fluoro-resin. The silicon oxide-based interlayer dielectric film and organic polymer (A)-based interlayer dielectric film are herein collectively referred to from time to time as the "interlayer dielectric film."

The organosilane polymer of the present invention has polycarbosilane in the skeleton and exhibits a dry etching speed of $1/3$ at most, generally $1/5$ or less, the dry etching speed of the silicon-containing interlayer dielectric film and the organic polymer-based interlayer dielectric film under the plasma dry etching conditions. Therefore, the organosilane polymer of the present invention can function as an etching stopper or a hard mask.

In the present invention, the organosilicon polymer functions as an etching stopper when formed under the interlayer dielectric film and as a hard mask when formed on the interlayer dielectric film.

[0032]

Etching stopper

When the interlayer dielectric film is etched by an etching process, the interlayer dielectric film is first formed on the etching stopper and a mask film having openings is formed on this interlayer dielectric film to give a laminated structure. Various methods can be used for forming openings in the mask film. One method of forming openings in the mask film is a lithographic technique using visible rays, ultraviolet rays,

or electron beams and a photosensitive polymer (photoresist).

A specific pattern can be formed on the interlayer dielectric film by etching the interlayer dielectric film through the openings in the mask film. Either the wet etching or dry etching can be applied to etching the interlayer dielectric film. An electric circuit pattern is given as an example of the specific pattern formed on the interlayer dielectric film.

[0033]

The etching speed is preferably the same at any point on the interlayer dielectric film. However, the etching speed may vary by location due to unevenness in the etching gas concentration, flow rate, temperature, and the like in the case of dry etching and due to unevenness in the concentration and convection of the etching solution and unevenness in the temperature in the case of wet etching. For this reason, if the etching time at the location where the etching speed is the slowest is applied, the etching gas or the etching solution reaches the lowest layer of the interlayer dielectric film all over the film except for the location where the etching speed is the slowest and chemically reacts with the materials existing below the interlayer dielectric film.

If an etching stopper is formed under the interlayer dielectric film, the chemical reaction due to the etching gas or the etching solution in the layer below the etching stopper can be prevented. If the speed to etch the etching stopper is slower than the speed to etch the interlayer dielectric film, the thickness of the etching stopper to prevent the etching gas

or the etching solution from chemically reacting with the materials existing below the interlayer dielectric film can be reduced. For example, when a low induction insulation film is used as the interlayer dielectric film, a thin etching stopper is desirable since the relative dielectric constant of the interlayer dielectric film is larger than that of the etching stopper.

[0034]

Hard mask

In the case where the etching selection ratio of the interlayer dielectric film to the photoresist is insufficient, the case where the photoresist film thickness is too thin to resist etching of the interlayer dielectric film, and the other similar cases, the opening pattern in the photoresist is transcribed onto a hard mask with a high etching selection ratio and the etching operation is carried out using the opening pattern on the hard mask.

In this case, a hard mask is formed on the interlayer dielectric film. A mask film with openings is further formed on the hard mask to give a laminated structure. Various methods can be used for forming openings in the mask film. One method of forming the openings in the mask film is a lithographic technique using visible rays, ultraviolet rays, or electron beams and a photoresist.

A specific pattern can be formed on the hard mask by etching the hard mask through the openings in the mask film. Either the wet etching or dry etching can be applied to etching the hard

mask. An electric circuit pattern is given as an example of the specific pattern formed on the hard mask. After removing the photoresist by means of a dry method (ashing) or wet method (wet delamination), the interlayer dielectric film is etched using the circuit pattern transcribed onto the hard mask as a mask.

[0035]

Damascene structure forming method

The damascene structure is formed by forming a pattern of trenches or via-holes in the interlayer dielectric film, filling a circuit metal in the trenches or via-holes, and removing excessive metal by the chemical machine polishing (CMP) method. There are two methods for forming a damascene structure. One is a single damascene forming method wherein trenches and holes are separately formed, filled with a metal, and polished by CMP and the other is a dual damascene forming method wherein the process of forming trenches and holes, filling them with the metal, and polishing by the CMP is carried out simultaneously only one time for the of trenches and holes.

The structure obtained by the dual damascene forming method of the present invention is characterized by being composed of two insulation film layers with a layer functioning as both the etching stopper and the hard mask interposed between them. (see FIG. 2)

Such a laminated structure can be obtained by sequentially laminating the interlayer dielectric film formed by the plasma CVD method or the coating method, the etching stopper film

formed by the plasma CVD method or the coating method, and the interlayer dielectric film formed by the plasma CVD method or the coating method. Wiring trenches are formed in the first and second interlayer dielectric films by photolithographic and etching processes. A uniform surface can be obtained more easily with an increased etching process allowance by interposing the etching stopper film between the first and second interlayer dielectric films. Via-holes can be formed in the second interlayer dielectric film by transcribing the via-hole pattern onto the etching stopper film.

Wiring for circuit can be formed in the laminated structure after the photolithographic and etching processes by forming damascene grooves and/or via-holes, coating the damascene grooves and/or via-holes with a barrier metal, and filling the grooves and/or via-holes with copper.

[0036]

The etching stopper obtained in this manner is useful for fabrication of semiconductors such as LSI, system LSI, MPU, CPU, DRAM, SDRAM, RDRAM, and D-RDRAM due to its excellent resistance to the etching process.

[0037]

[Examples]

The present invention will be described in more detail by way of examples.

In the following examples and comparative examples, "parts" and "%" respectively refer to "parts by weight" and "wt%" unless otherwise indicated.

The film-forming compositions in the examples were evaluated using to the following method.

[0038]

Weight average molecular weight (Mw)

The weight average molecular weight (Mw) of the polymer was measured by gel permeation chromatography (GPC) under the following conditions.

Samples: 1 g of the sample was dissolved in 100 cc of tetrahydrofuran.

Standard polystyrene: Standard polystyrene manufactured by Pressure Chemical Company was used.

Apparatus: A high temperature high-speed gel osmosis chromatogram (Model 150-CALC/GPC™) manufactured by Waters Co. of the U.S.

Column: SHODEX A-80M™ (length: 50cm) manufactured by Showa Denko K.K.

Measurement temperature: 40°C

Flow rate: 1 cc/min

[0039]

Etching selection ratio

Coated films were etched using the following apparatus.

Etching apparatus: Unity II manufactured by Tokyo Electron Co., Ltd.

An etching stopper formed on a silicon wafer was etched using the above etching apparatus to determine the thickness (thickness A) that can be etched within a unit period of time. An insulation film formed on a silicon wafer was etched using

the above etching apparatus under the same conditioned as applied to the etching stopper to determine the thickness (thickness B) that can be etched within a unit period of time. The quotient B/A was evaluated as the etching selection ratio.

[0040]

Preparation of solution (1)

Poly(phenylsilylene-ethynylene-1,3-phenylene-ethynylene) was dissolved in cyclohexanone to obtain a 15 wt% solution. This solution is referred to as "Solution (1)".

The solution (1) was filtered through a Teflon filter with 0.2 μ m pore size to measure the relative dielectric constant of the coating film.

The relative dielectric constant was 3.0.

[0041]

Synthesis Example 1

77.04 g of methyltrimethoxysilane, 24.05 g of tetramethoxysilane, and 0.48 g of tetrakis(acetylacetonate)titanium were dissolved in 290 g of propylene glycol mono-propyl ether in a separable glass flask. The solution was stirred using a three-one motor and the temperature of the liquid was stabilized at 60°C. Next, 84 g of ion exchange water was added to the solution over one hour. After reacting the mixture for two hours at 60°C, 25 g of acetylacetone was added. The resulting mixture was reacted for 30 minutes and cooled to room temperature. 149 g of a solution containing methanol and water was removed by evaporation at 50°C to obtain the reaction solution (2).

The weight average molecular weight of the resulting hydrolysis condensate (either the hydrolyzate or its condensate or both) was 8,900.

[0042]

Example 1

The etching selection ratio of the etching stopper film made from the polycarbosilane synthesized in Synthesis Example 1 was evaluated using an MSQ low induction interlayer dielectric film (LKD-5109 manufactured by the JSR Corp.) as an insulation film under the etching conditions A, B, C, and D.

[0043]

The etching selection ratios were 6.0 under the etching conditions A, 5.8 under the etching conditions B, 6.3 under the etching conditions C, and 7.8 under the etching conditions D.

[0044]

[Effect of the Invention]

A coating film (interlayer dielectric film material) for semiconductor with only minimal damages produced by the etching process can be obtained by using the etching stopper or hard mask made from the organic polymer having a relative dielectric constant of 4 or less of the present invention.

[Brief Description of the Drawing]

[Figure 1]

FIG. 1 is a drawing schematically showing the structure an etching stopper.

[Figure 2]

FIG. 2 is a drawing schematically showing the dual damascene

structure.

[Explanation of Symbols]

- 1 Mask membrane
- 2 Insulation film
- 3 Etching stopper
- 4 First insulation film
- 5 Etching stopper
- 6 Second insulation film
- 7 Barrier film

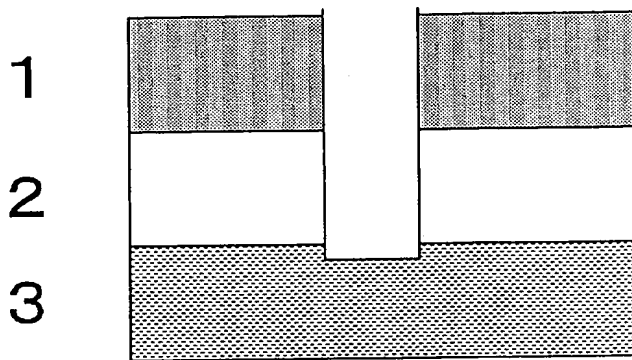


FIG. 1

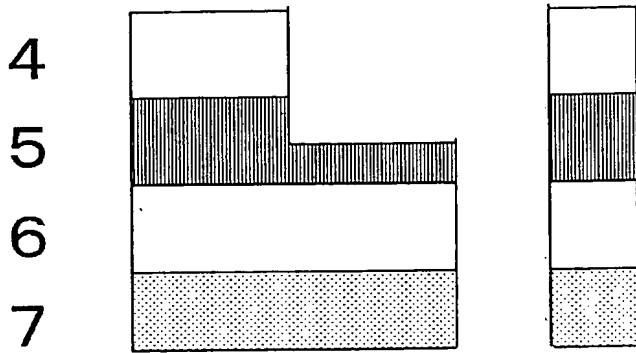


FIG. 2

[Document Name] Abstract

[Abstract]

[Subject] An etching stopper and hard mask suitably used for dry etching process of an interlayer insulation film made from silicon oxide, fluorine-doped silicon oxide, organic or inorganic spin-on-glass, or Low-k film, and dry etching process of a barrier film such as SiN, SiC, or SiCN.

[Means for the Solution] An insulation film comprising an organosilicon polymer with a relative dielectric constant of 4 or less and having a dry etching selection ratio to the compound selected from the group consisting of silicon oxide, fluorine-doped silicon oxide, organosilicate glass, carbon-doped silicon oxide, methyl silsesquioxane, or hydrogen silsesquioxane, a spin-on-glass, a polyorganosiloxane low dielectric interlayer insulation film, a Low-k (low dielectric interlayer insulation film), a polyorganosiloxane low dielectric interlayer insulation film, and an organic polymers low dielectric interlayer insulation film.

[Selective Drawing] None

HISTORICAL INFORMATION ON APPLICANT

Identification No.	[000004178]
1. Date of Alteration	December 10, 1997
[Reason for Alteration]	Alteration of Name
Address:	2-11-24, Tsukiji, Chuo-ku, Tokyo
Name:	JSR Corporation
2. Date of Alteration	May 6, 2003
[Reason for Alteration]	Alteration of address
Address:	5-6-10, Tsukiji, Chuo-ku, Tokyo
Name:	JSR Corporation
3. Date of Alteration	May 19, 2003
[Reason for Alteration]	Alteration of Name
	Alteration of address
Address:	5-6-10, Tsukiji, Chuo-ku, Tokyo
Name:	JSR Corporation
4. Date of Alteration	June 27, 2003
[Reason for Alteration]	Alteration of Name
Address:	5-6-10, Tsukiji, Chuo-ku, Tokyo
Name:	JSR Corporation